Efficient 1-Hexene Trimerization with Triazacyclohexane Chromium Catalysts and Detailed Product Analysis by ^{13}C NMR

Alexander G. N. Coxon, Randolf D. Köhn*

University of Bath, Department of Chemistry, Claverton Down, Bath, BA2 7AY, United Kingdom.

RECEIVED DATE (automatically inserted by publisher); E-mail: r.d.kohn@bath.ac.uk

Abstract:

Triazacyclohexane chromium pre-catalysts are described which catalyze the selective trimerization of 1-pentene, 1-hexene and 1-octene with unprecedented activity reaching nearly 5000 turnovers in an hour. The isomer distribution of the trimers has been analyzed in detail by application of quantitative ^{13}C NMR spectroscopy to ^{13}C labeled samples. All *endo*-cyclic elimination products predicted by the metallacyclic mechanism have been characterized and many confirmed by their independent synthesis. Significant variations in the isomer distribution are observed on variation of the ligand bulk. Quantification gave considerable insights into the relative abundance of metallacyclic intermediates, with 1,3-substituted chromacyclopentanes by far the most abundant resting state. Ring expansion selectivity favors 1,2 insertion into the less hindered Cr-C bond but some 2,1 insertion products have also been identified.

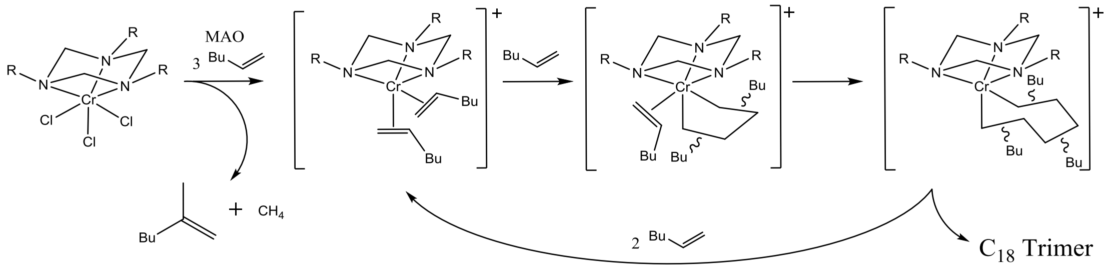
Keywords: selective olefin trimerization – catalysis - chromium – ^{13}C NMR characterization – metallacycle - oligomerization

Introduction

Highly selective ethylene trimerisation has been performed with a wide range of catalysts to produce 1-hexene as a precursor to linear low density polyethylene (LLDPE).[1,2] This process has been thoroughly investigated using various well-defined homogeneous catalysts that demonstrate excellent activities.[1,3-5] Since commercialisation in 2003 however, the focus of research into this process has shifted towards better understanding the mechanism.[6] It is now broadly accepted that the selective trimerization of ethylene is achieved *via* a metallacyclic mechanism, as indicated by deuterium scrambling and computational investigations.[7-10]

Despite the interest in trimerisation catalysts there has been only very limited progress in expanding their scope to include α-olefins.[11] Larger (C_9-C_{20}) α-olefins are typically produced in excess of demand by non-selective oligomerisation.[12] Trimerisation of these surplus products allows access to higher molecular weight hydrocarbons, which have been shown to exhibit highly favourable properties for application as synthetic lubricants.[13] Light (C_3-C_6) α-olefins are also readily available from various sources including dehydrogenation of alkanes present in natural gas, petroleum cracking and shale retort gas.[12] Trimerization of this range leads to highly branched hydrocarbons suitable for use as gasoline additives (C_3) or kerosene fuels (C_4-C_6).

While non-selective hexene oligomerization with a maximum at trimers (up to 77%) has been reported for some group 4 catalysts[14], the selective trimerisation of α-olefins was first reported by Köhn *et al.* in 2000 as part of their study of MAO (methylaluminoxane) activated (R_3TAC)$CrCl_3$ (R_3TAC = 1,3,5-trialkyl-1,3,5-triazacyclohexane) catalysts.[11,15] To the best of our knowledge, this activity has only been reproduced by Bercaw *et al.* using a (FI)$TiMe_3$ (FI = N-(5-methyl-3-(1-adamantyl)salicylidene)-2′-(2′′-methoxyphenyl)anilinato) catalyst after stoichiometric activation with $B(C_6F_5)_3$.[11] In both cases the proposed mechanism is analogous to that of ethylene trimerisation but is not yet well supported by experimental observation, Scheme 1.

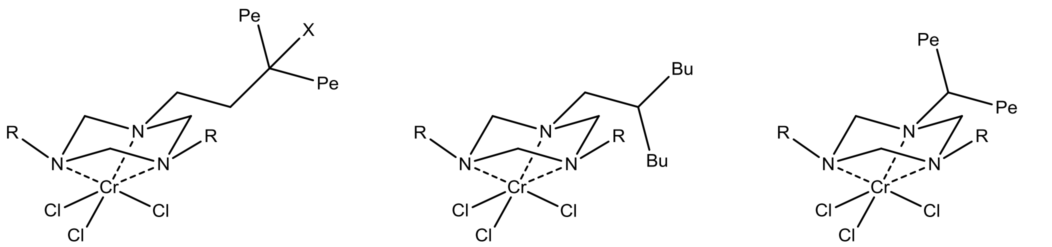


Scheme 1. An abbreviated representation of the proposed metallacyclic mechanism.

Contrary to ethylene, trimerisation of α-olefins leads to a range of isomers. Detailed analysis of the isomer distribution offers the potential to gain improved insight into the mechanism and stereochemistry involved, as well as the influence of ligand bulk variation. We report here significantly improved catalysts which enable mechanistic study into the proposed metallacyclic catalyst cycle for α-olefin trimerisation, based on analysis of the resultant trimeric regioisomers.

Results and Discussion

1-Hexene trimers were produced using four R_3TAC chromium catalysts of increasing bulk in the hope of inducing variation in the isomer distribution. Catalysts **1a** and **1b** have been described previously while the preparation of **1c** and **1d** is described herein.[16] Alkyl branched N-substituent catalysts are known to be effective ethylene trimerisation catalysts, while (2-ethylhexyl)$_3$TACCrCl$_3$ is the most effective α-olefin trimerisation catalyst reported to date.[13] Therefore, non-chiral catalysts of this type were synthesised as promising candidates for application to α-olefins.



(Pe$_2$(X)CCH$_2$CH$_2$)$_3$TACCrCl$_3$ **1a (X=H), 1b (X=Cl)** (Bu$_2$CHCH$_2$)$_3$TACCrCl$_3$ **1c** (Pe$_2$CH)$_3$TACCrCl$_3$ **1d**

Figure 1. The catalysts in order of increasing steric bulk. Where R indicates repetition of the shown N-substituent and Pe = pentyl.

All four catalysts, Figure 1, were active towards 1-hexene trimerisation although increased bulk led to reduced activity and turnover numbers. This is in line with previous observations on the effect of N-substituent branching point variation.[13] As predicted, the ((Pe$_2$(X)CHCH$_2$CH$_2$)$_3$TAC)CrCl$_3$ catalysts were most effective and demonstrated turnover numbers a factor of ten higher than the only alternative α-olefin trimerisation system reported to date.[11]

Table 1. 1-Hexene trimerisation efficiencies for the range of catalysts.

Catalyst	Conversion[a] (mol%)	Selectivity[b] (mol%)	Initial Activity[c] (Kg mol(Cr)$^{-1}$ h^{-1})	Turnover Number
1a	95	94	81	4437
1b	94	94	68	4473
1c	57	80	36	2273
1d	32	79	25	1257

[a] Proportion of 1-hexene consumed. [b] The quantity of C_{18} trimer formed as a proportion of the total products. [c] As measured by integration of ^{1}H NMR spectroscopy after 1 hour.

The results included in Table 1 were produced *via* an optimised procedure, described below, which led to a highly reliable system. Turnover numbers of around 4500 represent a significant improvement over previous TAC based α-olefin trimerization catalysts.[13] This is likely a result of the high solubility of **1a,b** in *ortho*-difluorobenzene (*o*-$C_6H_4F_2$) both before and after activation, which had presented problems for previous catalysts. *o*-$C_6H_4F_2$ is utilised as a solvent due to its polarity and hydrophobic nature, which enables dissolution of the ionic catalyst whilst remaining miscible with 1-hexene. These catalysts have also demonstrated considerable improvements in the stability of the activated catalyst, with minimal loss in activity when addition of 1-hexene was delayed by up to 24 hours.

The almost identical results observed for **1a,b** indicate the absence of any beneficial internal 'halogen effect', as observed for comparable ethylene systems.[16] However, the notable difference in initial activity does suggest that the chlorine present in the N-substituent is not entirely innocent and that it interferes with the catalyst cycle in a manner not yet understood.

The selectivity of each catalyst towards trimerization as compared to alternative oligomerization processes is consistent at >99 w% under all conditions investigated. The oligomeric selectivity was measured using GC-MS/FID analysis for 1-octene trimerization in order to be able to capture also all monomeric and dimeric by-products quantified using biphenyl as an internal standard. This method led to observation of trace quantities of C_{12} dimeric products (mixture of at least six different isomers giving a total of <0.1w% compared to trimer) for the first time, while no evidence of tetramerization could be detected. The content of dimer was too small to identify the isomers by NMR. Data base comparison for the GC-MS fragmentation patterns suggest a range of internal and vinylidene olefin dimers.

In addition, each of the catalysts investigated demonstrated a varying propensity to isomerize 1-hexene to 2-hexene, which accounts for the remaining loss in selectivity. The presence of 2-hexene has no effect on the catalysis, as tested by doping, and there is no sign of its incorporation into the trimer. In addition to observation of only trace quantities of 3-hexene; this would suggest that the catalysts are exclusive to linear α-olefins. Quantification of all volatiles vacuum transferred off the 1-octene trimerization reaction by NMR and GC-MS showed C8 products composed of 2% remaining 1-octene, 2% trans-2-octene, 1% cis-2-octene and 1% 2-ethyl-1-hexene (94% trimer). The latter octene isomer was already part of the commercial 1-octene while most of the 2-octenes was formed during the trimerization reaction. This trace analysis also shows that 2-ethyl-1-hexene (and probably vinylidene olefins in general) is not converted by the catalyst. When discounting these C8 isomers, the selectivity towards trimerization can be estimated at 99.9% of all oligomers. This selectivity is attributed to the greater steric bulk of internal olefins by analogy to the significant reductions in reaction rate seen on increasing the ligand bulk.

Product Identification

In order to characterise the isomer mix within the trimer product; ^{13}C enriched 1-hexene with ^{13}C at either the 1 or 2 position was synthesised according to modified published techniques.[17,18] The presence of three enriched carbon atoms in each of the trimers enabled detailed analysis by 1D ^{13}C and 2D ^{13}C-^{13}C COSY NMR spectroscopy. These techniques allowed the six key positions (labelled a-f in Figure 2), contained within the ring of the chromacycloheptane intermediate, to be identified for each isomer. Comparison of observed chemical shifts and ^{13}C-^{13}C coupling constants with known experimental results allowed the assignment of each isomer.

The regioisomers identified are all fully accounted for by the metallacyclic mechanism proposed by Köhn *et al.*[15] However, it is notable that no regioisomers were identified which exhibit unsaturation outside of the chromacycloheptane carbon chain as no ^{13}C signals greater than 0.5% were detectable which cannot be assigned to the *endo*-cyclic elimination products. It was predicted in the original proposal that a considerable proportion of the products would result from *exo*-cyclic β-hydride shift. The absence of these isomers indicates that this is not the case and there is instead a considerable preference for *endo*-cyclic elimination.

The observed isomers can be divided into a group of major isomers (A-E) for which all ^{13}C NMR signals could be assigned and a group of minor isomers (F-M) for which some signals overlap with those of more abundant isomers. However, the six key positions could be identified in all cases.

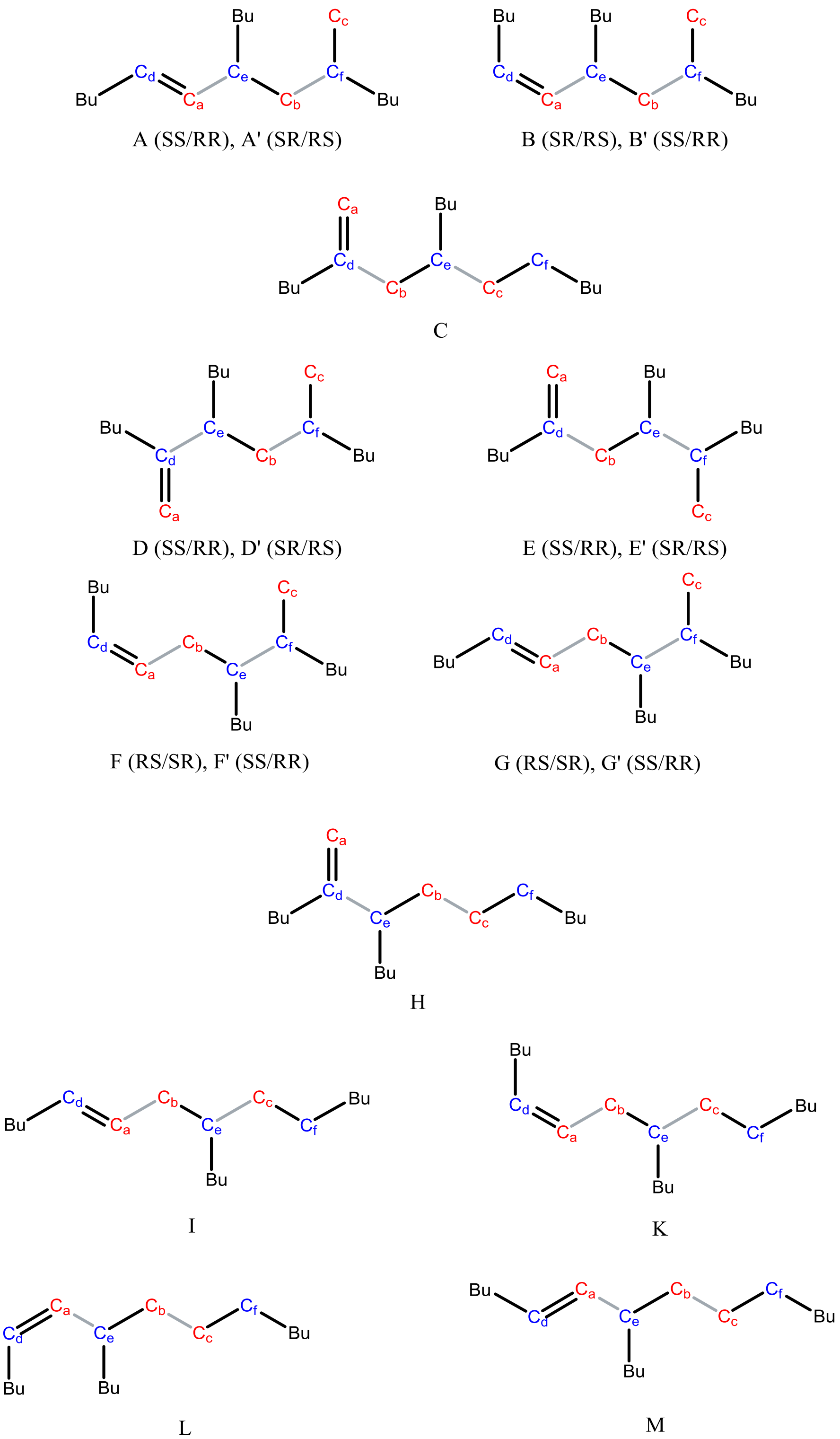


Figure 2. The characterised ^{13}C-labelled trimers. Chiral olefins will be racemates. Enriched positions are highlighted in red ($C_{a\text{-}c}$) for 1-^{13}C-1-hexene trimerisation products and blue ($C_{d\text{-}f}$) for 2-^{13}C-1-hexene trimers. The three enriched carbons of each labelling pattern are labelled in order of up-field shift based on their corresponding ^{13}C NMR spectra . Bonds coloured black are retained from the monomer units while bonds coloured grey are formed during catalysis.

Table 2. The observed enriched ^{13}C NMR shifts (ppm) of the regioisomers identified in dilute $CDCl_3$ and the coupling constants (Hz) between them.

Isomer	C_a	J_{ab}	C_b	J_{bc}	C_c	J_{ac}
A	135.04	1.5	43.20	0.5	19.25	<0.1
A’	135.39	1.5	43.51	<0.1	20.43	<0.1
B	135.50	1.3	44.00	0.1	20.48	<0.1
B’	135.18	1.3	43.62	0.4	19.60	<0.1
C	110.00	2.2	41.32	<0.1	33.47	<0.1
D	108.41	2.6	42.27	<0.1	20.31	<0.1
D’	108.84	2.5	41.50	0.4	19.52	<0.1
E	110.09	2.3	36.90	2.8	15.44	<0.1
E’	110.11	2.1	38.27	1.1	15.17	<0.1
F	129.65	43.1	27.69	2.8	15.654	<0.1
F’	129.49	43.1	28.99	1.4	15.561	<0.1
G	130.01	43.5	33.28	2.8	15.645	<0.1
G’	129.85	43.6	34.57	1.3	15.463	<0.1
H	108.50	2.5	34.17	35.1	27.54	<0.1
I	128.67	43.6	36.60	<0.1	33.47	2.4
K	128.32	43.1	31.26	<0.1	33.62	2.5
L	135.02	<0.1	36.00	35.1	27.40	1.6
M	135.09	1.0	35.64	35.5	27.28	1.7

Isomer	C_d	J_{de}	C_e	J_{ef}	C_f	J_{df}
A	129.98	0.49	40.44	0.72	30.03	<0.1
A’	129.73	0.49	40.28	0.73	29.94	<0.1
B	129.11	0.23	34.68	0.73	30.32	0.04
B’	129.46	0.27	34.80	0.76	30.29	0.06
C	149.14	1.92	35.23	0.92	26.53	<0.1
D	153.10	40.87	44.10	0.68	30.23	1.79
D’	152.40	40.87	44.56	0.70	30.11	1.27
E	149.41	1.73	39.63	34.88	33.53	2.69
E’	149.33	1.94	39.58	34.95	33.54	1.93
F	130.22	3.11	43.04	34.87	34.20	<0.1
F’	130.31	3.14	43.03	34.96	34.19	<0.1
G	131.19	3.18	42.61	34.91	34.12	<0.1
G’	131.20	3.18	42.71	34.93	34.08	<0.1
H	152.75	40.87	46.77	3.818	cc30.25	<0.1
I	131.63	3.09	37.78	0.75	27.37	<0.1
K	130.61	3.18	38.10	0.91	26.82	<0.1
L	129.48	0.32	37.12	3.75	29.90	<1
M	129.95	0.51	42.80	3.62	29.79	<1

cc: identified by CC COSY cross peak.

Differentiation and characterization of the diastereomers shown in Table 2 was achieved by comparison with literature data for related compounds of known stereochemistry and prediction with simple molecular mechanics modelling.[19] Details are given in the Supplementary Information. The carbon atoms of the butyl chains were also identified by matching fitted peak integrations and observed ^{13}C-^{13}C coupling. This gave considerable information into the chemical shifts of carbon atoms in branched olefins, which are currently poorly calculated by prediction software.[20] Complete assignments can be found in the Supplementary Information.

It was found that the observed ^{13}C NMR signals show a significant solvent and concentration dependence. As a result, many overlapping signals could be resolved by variation of the concentration and this provided additional support for the assignment. However, the unequivocal assignment of the isomers in different samples is therefore difficult as the relative position of some signals exchange on variation of the concentration or solvent ($CDCl_3$ and C_6D_6). Thus, we conducted a detailed study into the concentration dependence of different peaks and have successfully fit the signals to an empirical expression. Full details and calculations are provided in the Supplementary Information. This study provides reliable and accurate ^{13}C NMR shifts at both neat and infinite dilution for a large range of hydrocarbon environments. This information is seldom reported in the chemical literature but is essential, if NMR prediction software is to be improved.

The assignment of the spectra was further confirmed by specific synthesis of a mixture of isomers A and B. It was found that the spectra of all four isomers matched exactly to the peaks previously assigned to them. The *cis* (B) and *trans* (A) isomers of the synthesised product could be distinguished quantitatively due to the Z-selective Wittig reaction used during synthesis. Isomer C is known and has been fully characterised by ^{13}C NMR, with the assignments reported matching those presented here.[21] A mixture of L and M was also synthesised in order to confirm the assignment of some minor isomers. As above, the stereo selective Wittig synthesis applied allowed the assignment of both.

As shown in Figure 2, consecutive enriched carbons are all situated within a two or three bond separation from one another. The close proximity enabled the observation of spin-spin couplings between them and facilitated characterisation on comparison with literature values.[22] $^2J_{CC}$ and $^3J_{CC}$ couplings, regardless of the hybridisation of the carbons, were small at less than 4 Hz in each case. No couplings beyond $^3J_{CC}$ were observed indicating coupling constants of less than 0.1 Hz.

The labelling also resulted in observed $^{1\text{-}3}J_{CC}$ couplings between enriched and non-enriched carbons for the major isomers. $^1J_{CC}$ couplings were significantly affected by the hybridisation of the carbon atoms involved. The observed constants again matched those expected at 70-74 Hz for sp^2-sp^2, 40-44 Hz for sp^3-sp^2 and 34-36 Hz for sp^3-sp^3.[22] The presence of $^1J_{CC}$ coupling between enriched carbon atoms resulted in more complex splitting patterns. The significant difference in coupling intensity between $^1J_{CC}$ and $^{2/3}J_{CC}$ led to clearly identifiable doublets of doublets. This gave greater information into the connectivity and bond separation of the labelled atoms and facilitated identification of the isomers without access to information on the unlabelled carbon atoms. The complete set of coupling constants along with observed small ^{13}C isotope effects on the shifts is available in the Supporting Information.

Assignment of the ^{13}C chemical shifts for the different isomers *via* the labelling experiments enabled the facile identification of the products for non-enriched samples. Fitted-peak integration of up to 18 corresponding signals observed during quantitative ^{13}C NMR allowed statistically reliable calculation of the relative isomer abundance for each of the four catalyst systems, Table 3. The regioisomers have been split into four groups, each of which represents the products that are formed from the same metallacycloheptane intermediate, Scheme 2. GC-MS/FID was also investigated as a means of quantification and peaks corresponding to the major isomers were successfully correlated with NMR spectroscopy data, see SI. However, this method proved less effective as complete separation of such similar species could not be achieved.

Table 3. The regioisomers produced on trimerisation of 1-hexene across the catalyst range. Full details on the relative abundance of diastereomers is available in the Supplementary Information.

	Regioisomer Abundance (%)										
Catalyst	A	B	C	D	E	F	G	H	I	K	L	M
1a	39.9	22.4	11.8	16.5	3.6	2.0	0.9	0.4	0.2	1.2	0.4	0.7
1b	38.5	19.2	15.5	15.6	3.7	1.9	0.8	0.6	0.2	1.5	0.4	1.4
1c	46.9	15.3	3.0	19.7	8.3	3.1	1.5	0.3	0.2	0.7	0.3	0.7
1d	36.9	28.8	1.6	19.8	9.1	2.2	0.7	0.1	<0.1	0.4	<0.1	0.3

	Group Abundance (%)			
Catalyst	A-C	D-E	F-H	I-M
1a	74.1	20.1	3.3	2.5
1b	73.2	19.3	3.3	3.5
1c	65.2	28.0	4.9	1.9
1d	67.3	28.9	3.0	0.7

The use of 1-pentene and 1-octene as substrates was also thoroughly investigated in order to assess the effect of chain length variation on the product distribution. As shown in Figure 3, increases in the length of the alkyl tail had no notable effect on distribution, confirming 1-hexene as a suitable model for similar LAOs. Characterisation of the 1-pentene and 1-octene trimers was achieved using ^{13}C NMR spectroscopy by comparison to the C_{18} assignment and application of the increments devised by Grant and Paul (see SI).[23] The mechanistic insights described herein are therefore fully comparable to those of Bercaw *et al.* and the 1-pentene system they describe.[11]

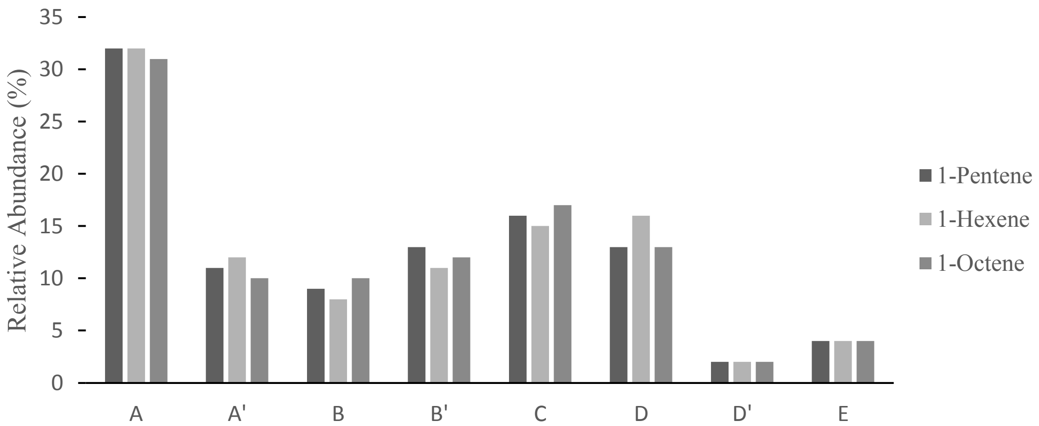


Figure 3. The effect of chain length variation on the relative isomer distribution of the eight major isomers.

Additional isomers of low abundance were observed in some cases where extended reaction times were employed. These products can be shown to result from isomerization of the initial trimers by exposure of isolated trimer to the catalyst solution. About 5% of the vinylidene trimers (C, D, E and H) are converted to internal tri-substituted olefins after 8 days. The new isomers were not further characterized but match many of the remaining unidentified minor peaks.

Insights into the Metallacyclic Intermediates

Characterisation of all significant isomers along with their relative abundance allowed insight into the predominant intermediates and pathways of the proposed metallacyclic mechanism. The proposed resting state of the catalytic cycle is the chromacyclopentane intermediate, of which there are three possible regioisomers, Figure 4.[7,24]

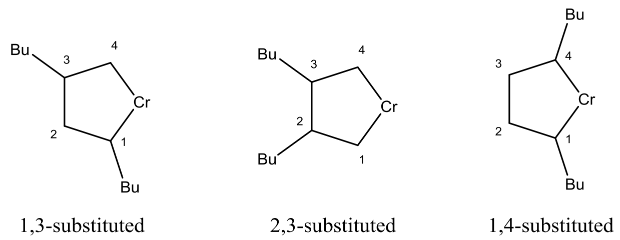
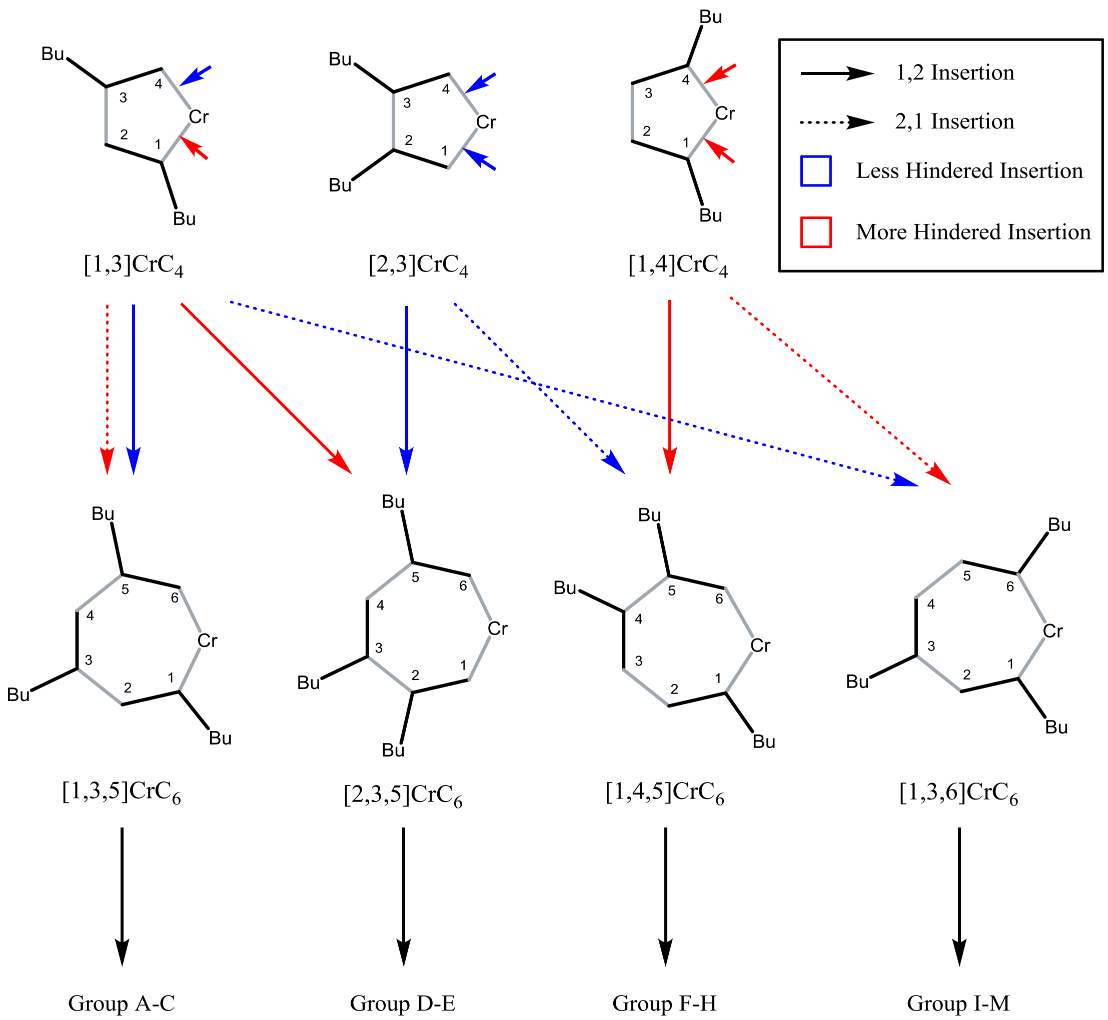


Figure 4. The three possible chromacyclopentane intermediates.

The chromacyclopentane formed is determined by the orientation of the α-olefin at the point of oxidative cyclisation.[15] It is therefore likely that the selectivity at this point is determined principally by steric factors, either between the butyl groups themselves or their interaction with the ligand. The relative abundance of these intermediates can be proposed based on the distribution of regioisomers produced.



Scheme 2. The possible pathways for insertion into the chromacyclopentane and the resulting product grouping. Bonds coloured black are retained from the monomer units while bonds coloured grey are formed during catalysis.

When looking at the intermediates formed during the catalytic cycle the products can be broken up into four groups, as shown in Scheme 2. Isomers in the same group are produced from the same chromacycloheptane intermediate and are differentiated by the β-hydride shift pathway. Based on the assumption that the major products, A-E, are only formed from 1,2-migratory insertion of the third α-olefin, there are only three pathways that lead to the bulk products.

Group A-C is solely accounted for by [1,3]CrC_4 and therefore directly correlates to the minimum abundance of this intermediate. This group constitutes the majority (>60%) of trimer product for each of the four catalysts. [1,3]CrC_4 appears therefore to be by far the most favoured chromacyclopentane, which in turn suggests steric hindrance between the butyl groups is of more significance than interaction with the ligand. Assuming 2,1-insertion to be a minor process, the abundance of this group also demonstrates a considerable preference for insertion into an un-substituted Cr-C bond, as shown by the ratio of A-C and D-E. The proportion of group A-C, and therefore [1,3]CrC_4, decreases as you move to bulkier ligands, suggesting that increased steric interaction between the butyl group at the 1-position and the ligand hinders its formation.

Group D-E can be formed from two possible pathways, either insertion into one of the Cr-C bonds of [2,3]CrC_4 or the more hindered Cr-C bond of [1,3]CrC_4. This prevents a definite conclusion on the preferred intermediate, though the highly favoured formation of [1,3]CrC_4 means it is likely that this leads to a considerable proportion of these products. The increasing relative abundance of D and E as the ligand bulk is increased suggests a shift from [1,3]CrC_4 towards the [2,3]CrC_4 intermediate. This strongly supports the existence of both intermediates as opposed to [1,3]CrC_4 alone. The suspected effect of ligand bulk on metallacycle formation can be estimated by DFT calculation[25] of the relative stability of all possible metallacycles for model (Me_3TACCr(propene)$_2$..$AlMe_4$] versus ($^tBu_3$TACCr(propene)$_2$..$AlMe_4$]: Boltzmann distribution at 298K would result in 50% [2,3]CrC_4, 45% [1,3]CrC_4 and 5% [1,4]CrC_4 for methyl substituents changing to 97% [2,3]CrC_4, 3% [1,3]CrC_4 and no [1,4]CrC_4 for tert-butyl substituents.

The observation of Group I-M at ~2.5% abundance indicates that 2,1 insertion accounts for a notable proportion of the products. It can be assumed that these isomers are formed almost entirely *via* [1,3]CrC_4 due to its much higher abundance relative to [1,4]CrC_4, as gauged by the low abundance of Group F-H. In turn, the contribution of 2,1 insertion into the hindered bond of [1,3]CrC_4 likely accounts for a minute proportion of A-C formed. As a result it can be estimated that 1,2 insertion is preferred over 2,1 insertion at an approximate ratio of 30:1. The decreasing abundance with greater ligand bulk agrees with the proposed preference for [2,3]CrC_4 in a more hindered environment.

Based on this ratio, up to 20% of Group F-H could be accounted for by 2,1 insertion into [2,3]CrC_4. The ~3.5% abundance of F-H therefore exaggerates the abundance of the [1,4]CrC_4 intermediate and shows it to be strongly disfavoured in comparison to the alternative chromacyclopentanes which is also supported by the DFT estimate described above. This suggests that while one butyl group adjacent to the chromium is capable of orientating itself away from the ligand bulk this is not possible when both are positioned in this way.

These results have shown that the steric bulk of the ligand has considerable influence over the selectivity of chromacyclopentane formation. Thus, the results show that the isomer distribution can be significantly changed by ligand design. This likely accounts for the stark difference in trimerisation selectivity between this system and that described by Bercaw *et al.*, which is highly selective for isomer D.[11] The considerably more bulky ligand motif used for this catalyst likely favours the formation of [2,3]CrC_4, which would lead to D as the majority isomer as observed in this study.

Conclusion

The chromium triazacyclohexane catalysts described herein have been shown to be highly active for α-olefin trimerisation. The least sterically hindered systems demonstrate turnover numbers and activities that far exceed those of any other known system as well as selectivities of around 95%.[11]

Extensive ^{13}C labelling studies led to the characterisation of each constituent regioisomer of the product mix down to an abundance of 0.1%. Every regioisomer, produced *via endo*-cyclic elimination, predicted by the previously proposed metallacyclic mechanism has been identified. These results strongly support its existence, and by implication, the analogous mechanism proposed for ethylene systems. However, the results have also shown that the proposed α-olefin mechanism requires modification, as the predicted *exo*-cyclic elimination pathways have not materialised.[15]

The location of the alkyl chains in the trimer provided significant insight into the metallacyclic intermediates of the catalyst cycle. [1,3]CrC_4 was identified as the predominant metallacyclopentane intermediate in all cases (>60%), along with a much lower abundance of [2,3]CrC_4 and [1,4]CrC_4 (<5%). This selectivity is predominantly under steric control, with interaction between adjacent butyl groups most important and ligand bulk having a lesser influence.

The detailed assignment of all regioisomers is an important resource for any future study of selective LAO trimerization. We are currently working on a study into deuterium isotope effects on the isomer distribution and detailed computational studies to rationalise the observed isomer distribution.

Experimental

All manipulations of air/moisture sensitive compounds were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques or a Saffron glove box. All reagents were obtained from major suppliers. 1,2-difluorobenzene was degassed under vacuum before being stored over molecular sieves in an argon atmosphere. Other dry solvents were obtained from the Innovative Technology Solvent Purification System (SPS).

Instrumentation and Characterization Procedures

NMR spectra were obtained on either a Bruker DRX500 MHz FT-NMR spectrometer [500MHz (^{1}H), 125MHz (^{13}C), 51MHz (^{15}N)], or a Bruker DRX400 MHz FT-NMR spectrometer [400MHz (^{1}H), 100MHz (^{13}C)] at 298K. All ^{13}C spectra are H decoupled. Shift values are quoted in ppm relative to internal TMS or external liq. NH_3 (^{15}N). Coupling constants and line widths (W) are quoted in Hz. J-coupling is $J_{H\text{-}H}$ for ^{1}H NMR spectra and $J_{C\text{-}C}$ for coupled ^{13}C NMR spectra unless otherwise stated. Effective magnetic moments were measured using the Evans method and corrected for the diamagnetic contribution.[26,27]

The T_1 relaxation times of all carbon atoms within the trimer were observed to be 3 seconds (quaternary C in vinylidene) or less for neat hexene trimers, such that acquisition delays of 15 seconds allowed quantitive analysis of the trimer mix by inverse gated decoupling. The longest T_1 increases to 6 seconds for neat pentene trimers (30s delay) and more than doubles in dilute $CDCl_3$ or C_6D_6 solutions, making quantitative measurements less favourable. The longest T_1 in neat octene trimer was found to be 1s. All integrations were measured using Gaussian fitting of the curve to ensure reliability. Acquisition times of 5s and exponential multiplication with a line broadening factor of 0.2 Hz gave spectra with typical signal widths of 0.5 Hz.

Mass spectra were obtained using a Bruker Daltonik micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer using acetonitrile as a solvent. All data was collected using cation detection. The peaks quoted correspond to the calculated exact mass, the correct isotope patterns are present where the peak is quoted. For metal complexes a small amount of $Me_3N.HCl$ was added to observe predictable ion formation ($[M+C_3H_{10}N]^+$) unless otherwise stated.

Elemental analysis was performed by London Metropolitan University Elemental Analysis Service, UK.

GCMS analysis was performed with an Agilent 7890B with Agilent 5977A MSD and FID detectors. A DB-FFAP column 30 m in length, with a diameter of 0.250 mm and a 0.25 µm film thickness was used in all cases. A ramp rate of 3°C per minute was used from 40°C to 350°C.

Synthesis of the mixture of isomers A, A’, B and B’ and of a mixture of L and M is described in the supplementary information.

Synthesis of **1c**

Under nitrogen, NaOMe (24.7 g) was dissolved in dry methanol to give a 200 mL solution and added into a dropping funnel. 100 mL of this solution was run into a 10 mL methanol solution of ethyl cyanoacetate (24.4 g) and stirred for 1 hr at room temperature to give a yellow solution. The first portion of 1-bromobutane (25 mL) was added *via* pipette and the reaction heated to 40°C for 1hr, then 50°C for 1hr and finally 60°C for 1hr before being cooled to room temperature. A light precipitate formed after 30 min at 40°C. The remaining NaOMe solution was added to the reaction mixture and stirred for 15 minutes at room temperature. The second portion of 1-bromobutane (25 mL) was added and the reaction mixture heated to 60°C. The red mixture is decanted from any solids and concentrated *in vacuo* to give a large quantity of red solids. The mixture was extracted with 3 x 100 mL PET and the extracts concentrated *in vacuo*. The remaining red liquid was transferred at 0.02 mbar and ~300°C into a water-cooled receiving flask to give 33.8 g of a colourless clear liquid (159 mmol, 74%). ^{1}H NMR (500 MHz), $CDCl_3$: δ = 3.75 (3H, s), 1.84 (2H, td, J = 12.8 / 4.7), 1.72 (2H, td, J = 12.8 / 4.3), 1.48 (2H, m), 1.28 (4H, m), 1.23 (2H, m), 0.856 (6H, t, J = 7.3). ^{13}C NMR (125 MHz), $CDCl_3$: 169.65, 119.19, 52.94, 49.71, 37.08, 27.33, 22.15, 13.47.

LiCl (22.84 g), water (4 mL) and DMSO (100 mL) were added to the ester (33.67 g). The mixture was heated to 155°C under nitrogen for 2 days. The brown mixture was cooled to 25°C and 200 mL water and 150 mL pentane was added. The aqueous phase was separated and the organic phase washed with 4x 100 mL water. The remaining organic phase was filtered through $MgSO_4$ and the solvent removed under vacuum before being transferred at 10^{-3} mbar and ~300°C into an ice cooled flask (21.42 g colourless liquid, 140 mmol, 88%). ^{1}H NMR (500MHZ), $CDCl_3$: δ = 2.48 (1H, tt, -C**H**CN), 1.57 and 1.54 (4H, m, -C**H**$_2$Pr), 1.5 and 1.4 (4H, m, -C**H**$_2$Et), 1.34 (4H, sextet, -C**H**$_2$Me), 0.906 (6H, t, J = 7.0, -C**H**$_3$). ^{13}C NMR (125MHz), $CDCl_3$: δ = 122.33 (-**C**N), 31.88 (t, J = 127, -**C**H$_2$Pr), 31.52 (d, J = 134, -**C**HCN), 29.17 (t, J = 125, -**C**H$_2$Et), 22.12 (t, J = 126, -**C**H$_2$Me), 13.68 (qt, J = 127.7 / 3.7, -**C**H$_3$).

Solid $AlCl_3$ (11.15 g) is slowly added to 200 mL Et_2O cooled in an ice bath. When dissolved, solid $LiAlH_4$ (9.17 g) is added to give a grey suspension. The ice bath is removed and a solution of the nitrile in 50 mL Et_2O is added drop wise over 1 hr and left stirring overnight. The mixture is cooled in an ice bath and hydrolysed consecutively with 10 mL water, 10 mL 20% NaOH, 40 mL water and 20 mL of 20% NaOH followed by 100 mL Et_2O to replace evaporation losses. The mixture was stirred for 1 hr until white. The solution was decanted and combined with further Et_2O extracts (3x 100 mL), reduced under vacuum and transferred at 10^{-3} and 100°C into an ice cooled flask to give 20.63 g (131 mmol, 94%) clear colourless liquid. ^{1}H NMR, $CDCl_3$: δ = 2.59 (2H, d, J = 4.6, J_{CH} = 133.2, -C**H**$_2$NH$_2$), 1.28 (1H, m, -C**H**CH$_2$NH$_2$), 1.27 (4H, m, -C**H**$_2$Me), 1.26 (4H, m, -C**H**$_2$Et), 1.25 (4H, m, -C**H**$_2$Pr), 1.15 (2H, broad s, -N**H**$_2$), 0.88 (6H, t, J = 6.9, J_{CH} = 124.6, -C**H**$_3$). ^{13}C NMR, $CDCl_3$: δ = 45.21 (-**C**H$_2$NH$_2$), 40.85 (-**C**HCH$_2$NH$_2$), 31.20 (-**C**H$_2$Pr), 28.99 (-**C**H$_2$Et), 23.08 (-**C**H$_2$Me), 14.06 (-**C**H$_3$).

612 mg amine (3.89 mmol) was added to 119 mg paraformaldehyde (3.96 mmol) with 10 mL toluene and stirred for 1 day. The solvent was removed at 10^{-3}. The ligand was dissolved in pentane, filtered and the solvent removed again to give 610 mg TAC (1.2 mmol, 93%). ^{1}H NMR, $CDCl_3$: δ = 3.25 (6H, broad s, -NC**H**$_2$N-), 2.275 (6H, d, -C**H**$_2$N), 1.2-1.4 (39H, m, -C**H**C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.885 (18H, t, J = 6.8, -C**H**$_3$). ^{13}C NMR, $CDCl_3$: δ = 74.33 (-N**C**H$_2$N-), 57.14 (-**C**H$_2$N), 36.03 (-**C**HCH$_2$N), 32.06 (-**C**H$_2$Pr), 28.95 (-**C**H$_2$Et), 23.21 (-**C**H$_2$Me), 14.14 (-**C**H$_3$).

Under argon, the ligand (150 mg, 0.29 mmol) was diluted with PhF_2 and $CrCl_3(THF)_3$ (109 mg, 0.29 mmol) was added. A deep purple solution formed immediately and was left standing overnight. The solution was passed through a silica column with $CHCl_3$ and the purple band was collected, the solvent removed and the solids dried under high vacuum. 164 mg of a purple solid was isolated (84%). Magnetic moment (DCM) = 3.56 BM. ^{13}C NMR (125MHz), $CDCl_3$: δ = 45.1 (6C, W = 160, -**C**H_2Pr), 27.9 (6C, W = 91, -**C**H_2Et), 22.4 (6C, W = 68, -**C**H_2Me) 13.0 (6C, W = 63, -**C**H_3), -34.7 (3C, W = 790, -**C**HCH_2N). ESI-MS (m/z) $[C_{33}H_{69}Cl_3CrN_3.C_3H_9N]^+$: Calculated exact mass: 724.4775, found: 724.4761. *Anal.* Calc. for $C_{33}H_{69}Cl_3CrN_3$ (%):C, 59.49; H, 10.44; N, 6.31. Found: C, 59.47; H, 10.51; N, 6.41.

Synthesis of **1d**

2.00 g undecan-6-amine (11.67 mmol), prepared according to literature techniques,[28] was dissolved in 25 mL toluene before paraformaldehyde (345 mg, 11.5 mmol) was added and stirred overnight. The cloudy mixture was concentrated under high vacuum to give a cloudy oil. The oil is dissolved in pentane, filtered through $MgSO_4$ and the pentane removed to give 1.97 g of a clear oil (93% yield). NMR in $CDCl_3$(TMS) showed a mixture of R_3TAC and RN=CH_2 (about 1:2 by weight).
R_3TAC: ^{1}H NMR, $CDCl_3$: δ = 3.54 (6H, s, -NC**H**$_2$N-), 2.57 (3H, quintet, J = 5.3, -C**H**N), 1.47 (12H, m, -C**H**$_2$Bu), 1.2-1.3 (36H, m, -C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.89 (18H, t, 6.5, -C**H**$_3$). ^{13}C NMR, $CDCl_3$ (No decoupling): δ = 67.77 (t, J = 139.0, -N**C**H_2N-), 59.12 (d, J = 132.0, -**C**HN), 32.37 (t, 124.9, -**C**H_2Pr), 30.54 (-**C**H_2Bu, t, J = 126.1), 26.41 (t, J = 125.1, -**C**H_2Et), 22.81 (t, J = 124.8, -**C**H_2Me), 14.14 (q, J = 124.5, -**C**H_3). ^{15}N NMR, $CDCl_3$: δ = 49.1.
RN=CH_2: ^{1}H NMR, $CDCl_3$: 7.320 (trans) and 7.145 (cis) (2H, d, J = 17.4, =C**H**$_2$), 2.80 (1H, quintet, J = 6.25, -C**H**N), 1.53 (4H, m, -C**H**$_2$Bu), 1.2-1.3 (12H, m, -C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.87t (6H, t, J = 7.0, -C**H**$_3$). ^{13}C NMR, $CDCl_3$ (No decoupling): 151.14 (ddd, J = 177.4 / 157.5 / 6.9, =**C**H2), 73.61 (d, 131.3, -**C**HN), 35.85 (t, J = 124.9, -**C**H_2Bu), 31.79 (t, J = 125.0, -**C**H_2Et), 25.92 (t, J = 125.4, -**C**H_2Pr), 22.66 (t, J = 24.6, -**C**H_2Me), 14.08 (q, J = 124.5, -**C**H_3). ^{15}N NMR, $CDCl_3$: δ = 363.

The TAC/imine mixture is further dried in high vacuum/hot water bath for 2 hrs leaving 1.60 g of the dry mixture. In a glove box under argon, 415 mg of this mixture is added to $CrCl_3(THF)_3$ (293 mg) along with 2 mL PhF_2. After stirring overnight, the purple solution is passed through a short silica column with DCM. The solvent is allowed to evaporate to give a purple oil before the product is recrystallized from 20 mL Et_2O at -10°C. The colourless solution is decanted and the residue washed twice with 20 mL of pentane to give a purple solid, **1d**, after drying under high vacuum. ESI-MS (m/z) $[C_{36}H_{75}Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 766.525, found: 766.527. ^{13}C NMR (500MHz), $CDCl_3$: δ = 40.6 (6C, W = 172), 29.2 (6C, W = 67), 21.3 (6C, W = 40), 12.0 (6C, W = 28), -40.5 (6C, W = 1464). *Anal.* Calc. for $C_{36}H_{75}Cl_3CrN_3$ (%):C, 61.04; H, 10.67; N, 5.93. Found: C, 61.11; H, 10.73; N, 5.93.

Optimised α-Olefin Trimerization Procedure

2 mg of catalyst, 250 equivalents of DMAO and 7500 equivalents of dry *o*-$C_6H_4F_2$ are added to the reaction vessel under argon to form a green solution which is agitated until completely homogenous (~2 minutes). 5000 equivalents of Na/K dried 1-hexene is then added, resulting in a yellow-green solution, and the vessel left under an argon atmosphere for the entirety of the reaction. An NMR sample is taken after one hour to test the initial activity of the catalyst before being returned to the bulk solution. The reaction is complete after 6 hours.

The trimer is extracted from the reaction mixture by exposing the solution to air before the drop-wise addition of methanol. This results in significant effervescence and the formation of white precipitate. Once no further reaction is observed, several drops of hydrochloric acid are added to solubilise the alumina solids, resulting in further effervescence. This treatment results in the formation of a green 'aqueous' phase containing the aluminium and chromium species and a clear organic phase, which is collected.

The majority of the *o*-$C_6H_4F_2$ and hexenes are removed from the organic phase at 1 mbar and 40˚C. The remaining colourless liquid is transferred under high vacuum ($1x10^{-3}$ mbar) at ~200˚C across a short bridge to a receiving flask in a cold water bath. A liquid nitrogen cooled trap is used to collect any remaining volatile components. The pure trimer collected is then analysed by NMR in $CDCl_3$ doped with TMS.

Trimer Isomerisation

4.4 mg **1b** (0.0049 mmol) and 76 mg DMAO (1.3 mmol, 270 Eq. Al) are dissolved in 1522 mg *o*-$C_6H_4F_2$ to give a green solution, which is shaken until all solids are fully dissolved (5 minutes). 560 mg 1-hexene trimer (2.2 mmol, 450 Eq.) prepared using **1b** is then added to give a yellow-green solution and is left to stand for 8 days with NMR spectroscopy monitoring. The trimer was isolated as above.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ….
Description of quantitative product analysis run of 1-octene trimerization, synthesis of 1-^{13}C-1-hexene, 2-^{13}C-1-hexene, mixture of A+A'+B+B', mixture of L+M
Assignment of regio-isomers, IUPAC names of isomers, GC-MS of trimers, description of concentration dependence of trimer ^{13}C NMR spectra, isomer distribution details for all region-isomers and comparison to 1-pentene and 1-octene trimer distribution, increment table for change in NMR shifts from 1-hexene to 1-pentene and 1-octene trimer.
EXCEL spreadsheets with detailed NMR data for 1-pentene, 1-hexene and 1-octene trimers providing shifts at any concentration in $CDCl_3$ or C_6D_6, labelled ^{13}C trimer shifts and coupling constants.

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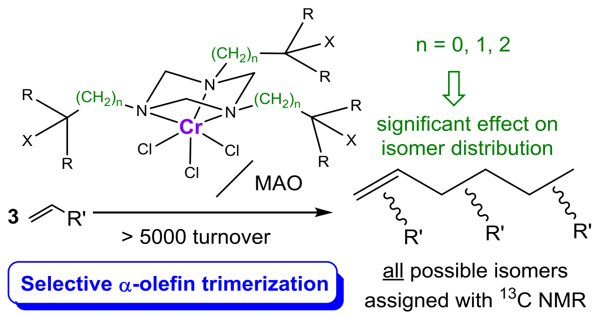

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